

# Chapter 1



## Introduction

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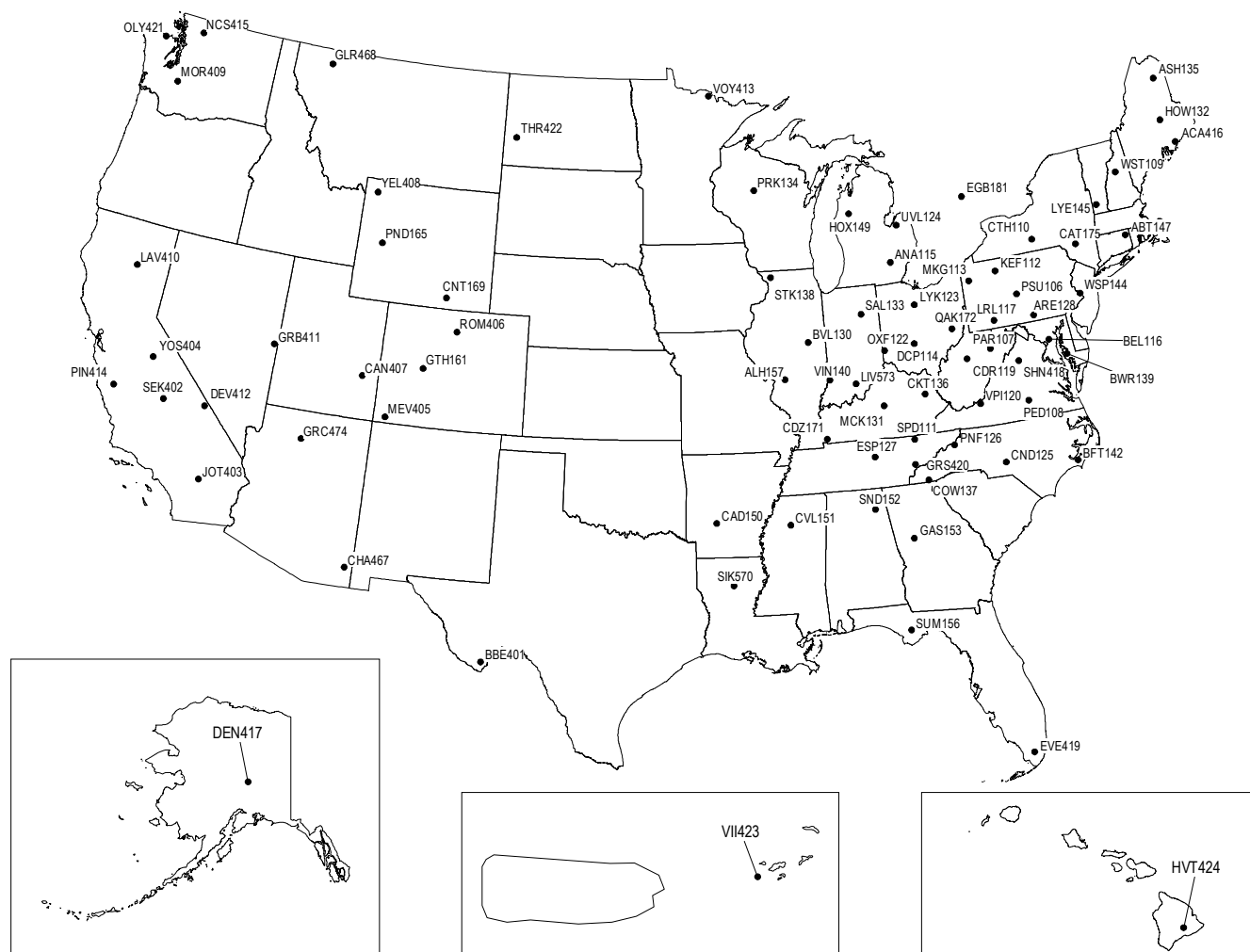
*A national monitoring network was mandated by the 1990 Clean Air Act Amendments (CAAA) to determine the effectiveness of promulgated emission reductions. The U.S. Environmental Protection Agency (EPA) established the Clean Air Status and Trends Network (CASTNet) to provide data for determining relationships between emissions, air quality, deposition, and ecological effects. CASTNet's objectives are to define the spatial distribution of pollutants, detect and quantify trends in pollutants, implement monitoring in cooperation with other agencies and organizations, and implement monitoring to fill gaps in monitoring coverage. This report summarizes the CASTNet monitoring activities and the resulting concentration and deposition data for 2000.*

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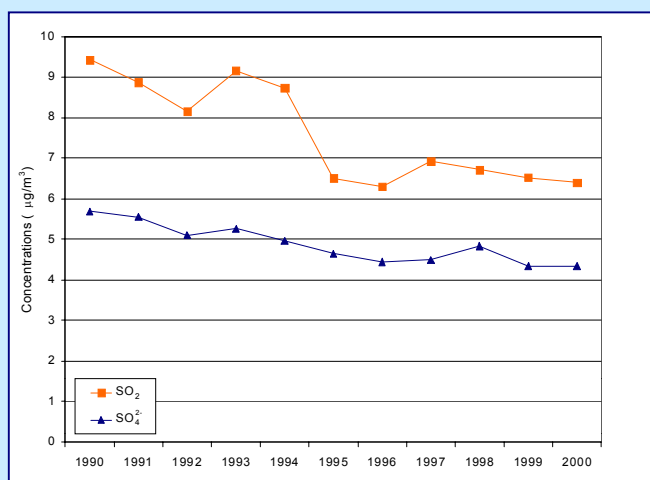
## CASTNet Overview

CASTNet's primary goal is to function effectively as a national, long-term deposition monitoring network that provides information for assessing the effectiveness of current and future emission reductions mandated under the Clean Air Act. To meet this goal, the CASTNet program was designed to: 1) monitor the status and trends in air quality and atmospheric deposition; 2) provide atmospheric data on the dry deposition component of total acid deposition, rural ground-level ozone, and other forms of atmospheric pollution that enter the environment as particles and gases; and 3) assess and report on geographic patterns and long-term, temporal trends in ambient air pollution and acid deposition.

*CASTNet is the principal source of information on dry deposition throughout the United States. Dry deposition is a component of acidic deposition, which occurs when emissions of sulfur dioxide ( $\text{SO}_2$ ) and oxides of nitrogen ( $\text{NO}_x$ ) react with particles, water droplets, oxygen, and oxidants to form acidic compounds. Dry deposition represents a variety of meteorological, chemical and biological processes that transport and deposit these acidic compounds to the environment. Wet deposition occurs when precipitation removes the acidic compounds from the atmosphere and deposits them to the environment.*

**Figure 1-1.** Locations of CASTNet Sites as of December 2000

SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> concentrations measured at 34 eastern reference sites have declined significantly over the period 1990 through 2000.



The principal component of CASTNet is the measurement of atmospheric sulfur and nitrogen pollutants at rural sites throughout the United States. Cation sampling was initiated in January 2000 to allow for a better understanding of the chemical balance of the collected particles and also for consistency with the precipitation chemistry measurements collected by the National Atmospheric Deposition Program/National Trends Network (NADP/NTN). Additionally, the network includes measurement of fine mass ( $PM_{2.5}$ ) and its chemical constituents at some sites. Almost all CASTNet sites include continuous measurements of ozone ( $O_3$ ) concentrations and meteorological conditions together with supporting information on vegetation and land use. The meteorological, vegetation, and land use data are used as input to the Multi-Layer Model (MLM), a mathematical model that simulates atmospheric dry deposition processes. The MLM, which has been described and evaluated by Meyers *et al.* (1998) and Finkelstein *et al.* (2000), is used to calculate deposition velocity ( $V_d$ ). The modeled  $V_d$  are combined with the concentration measurements to estimate dry deposition of pollutants.

Prior to CASTNet, EPA operated the National Dry Deposition Network (NDDN), which was established in 1986. As with CASTNet, the objective of the NDDN was to obtain field data to establish patterns and trends of dry deposition at approximately 50 sites throughout the United States. NDDN also estimated dry deposition using measured air pollutant concentrations and modeled  $V_d$ . NDDN was incorporated into CASTNet in 1991.

*EPA and the National Park Service (NPS) cosponsor CASTNet. During 2000, EPA operated 52 sites, mostly in the eastern United States, and NPS operated 27 sites at various national parks and monuments, mostly in western locations.*

NPS is responsible for the protection and enhancement of air quality related resources in national parks and wilderness areas. To carry out these responsibilities, NPS has developed an air quality program that involves a wide range of activities, including air quality monitoring and modeling, and participation in CASTNet. In 1994, under a partnership agreement with EPA, NPS merged 17 previously operating sites into the network and assumed operation of two other park sites. New sites have been added subsequently. NPS

and EPA are responsible for operating their sites under a common set of quality assurance (QA) standards and similar monitoring and data validation protocols. The measurements from the NPS and EPA sites are merged into a single database and delivered to EPA quarterly.

This report summarizes results of CASTNet monitoring activities for 2000. Included in this summary are annual and quarterly mean concentration data for atmospheric sulfur and nitrogen species and cations; estimates of wet and dry deposition with an analysis of trends in concentrations and deposition over the period 1990 through 2000;  $O_3$  data for 2000 and trends over the 11 years; concentrations of  $PM_{2.5}$  with time series analysis from 1994 through 2000; and an assessment of data quality. CASTNet Annual Reports for 1998 and 1999 (Harding ESE, 1999 and 2001a, respectively) can be found on the EPA web site: [www.epa.gov/castnet/reports.html](http://www.epa.gov/castnet/reports.html). These reports summarize network activities and data for each of those two years.

## Network Description

The locations of CASTNet sites, as of December 2000, are shown in Figure 1-1. Seventy-nine sites were operational. Seventy-seven of the 79 sites were equipped with filter packs for measurement of pollutant concentrations and estimation of deposition rates. Seventy-four sites measured  $O_3$ . Two dry deposition sites included collocated sampling systems for determining network precision. Appendix A provides the location and operational characteristics of each CASTNet site by state including information on site location, start date, latitude, longitude, elevation, and the types of measurements taken at the site. Also included is information on the type of surrounding terrain and land use, a designation regarding the representativeness of each site with respect to MLM modeling assumptions, and the sponsoring agency (EPA or NPS).

CASTNet included 8 sites that utilized aerosol filter packs to take visibility-related measurements. Six of these sites were collocated with dry deposition sites, and two sites also measured optical properties of the atmosphere. The Quaker City, OH (QAK172) site had collocated equipment for QA purposes.

**Table 1-1.** Significant Operational Events During 2000

<b>January</b>
The field calibration schedule was revised so all sites are visited during each of two five-month periods: January to May and July to November.
Analysis of cations (calcium, magnesium, sodium, and potassium) on the Teflon <sup>®</sup> filter was initiated.
An ion chromatograph (IC) was purchased by Harding ESE and became operational in the Gainesville analytical laboratory.
<b>February</b>
Work began on the development of a software package, the Data Management System application, with the goal of streamlining data ingestion and delivery processes.
<b>March</b>
Dr. Dave MacTavish, Manager of CAPMoN, performed an informal system review of the Gainesville analytical laboratory.
A second IC was purchased by Harding ESE and became operational in the Gainesville analytical laboratory.
<b>April</b>
Harding ESE Gainesville analytical laboratory discontinued analysis of the sodium carbonate denuders exposed at the visibility collocated site.
A collocated sampling system at the visibility site QAK172 became operational. Only a collocated nylon filter pack was operated at the site previously.
The collocated sampling system at the visibility site in Sikes, LA (SIK570) was discontinued.
<b>June</b>
Harding ESE hired a new Data Operations Manager for the Data Management Center.
<b>July</b>
The Data Management System application became operational.
The GAS153 site was moved about 0.5 miles from the old location.
<b>August</b>
Installation of uninterruptible power supplies for the ozone analyzers began for all CASTNet sites.
<b>September</b>
Replacement potentiometers were installed in the Climatronics wind direction sensors.
<b>October</b>
The Wellston, MI (WEL149) site was moved approximately 5.0 miles southeast to Hoxeyville, MI (HOX149).

The NADP/NTN performed wet deposition sampling at 15 CASTNet sites. This effort included analysis and reporting of precipitation chemistry samples. NADP/NTN operated wet deposition sampling systems at other locations near virtually every CASTNet site. The NADP/NTN database represents the primary source of information on wet deposition across the United States. The combination of CASTNet and NADP/NTN data provides information on total (dry + wet) deposition. More information about NADP/NTN may be found on their web site: <http://nadp.sws.uiuc.edu>.

One of the CASTNet sites is located in Egbert, Ontario, Canada (EGB181). At this site, day and night samples are collected weekly along with a standard weekly composite CASTNet filter pack. This setup provides the means to compare results from CASTNet with the Canadian Air and Precipitation Monitoring Network (CAPMoN). O<sub>3</sub> is not measured at EGB181.

Table 1-1 summarizes significant operational events and decisions for 2000. More details on the history of the network can be found in the CASTNet 1998 and 1999 Annual Reports (Harding ESE, 1999 and 2001a).

## Methods

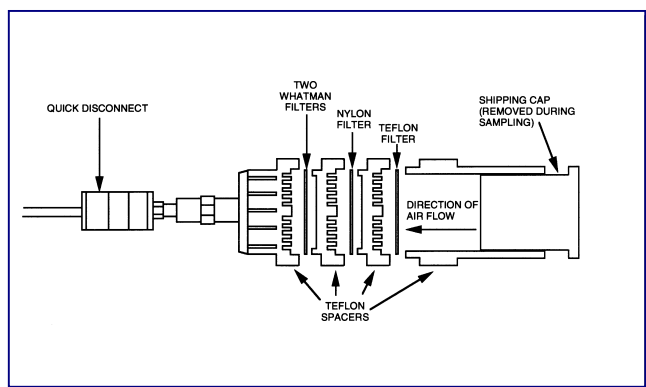
This section provides a brief overview of methods employed for CASTNet. Step-by-step protocols and additional details on these activities are found in the CASTNet Quality Assurance Project Plan (QAPP) (Harding ESE, 2001b) and previous annual reports.

### CASTNet ambient measurements include:

- sulfur dioxide (SO<sub>2</sub>)
- particulate sulfate (SO<sub>4</sub><sup>2-</sup>)
- particulate nitrate (NO<sub>3</sub><sup>-</sup>)
- nitric acid (HNO<sub>3</sub>)
- particulate ammonium (NH<sub>4</sub><sup>+</sup>)
- particulate calcium (Ca<sup>2+</sup>)
- particulate sodium (Na<sup>+</sup>)
- particulate magnesium (Mg<sup>2+</sup>)
- particulate potassium (K<sup>+</sup>)
- ozone (O<sub>3</sub>)
- meteorological variables and information on land use and vegetation.

## Field Operations

Meteorological variables and  $O_3$  concentrations were recorded continuously and reported as hourly averages. Atmospheric sampling for sulfur and nitrogen species was integrated over weekly collection periods using a three-stage filter pack (Figure 1-2). In this approach, particles and selected gases were collected by passing air at a controlled flow rate through a sequence of Teflon<sup>®</sup>, nylon, and Whatman filters. The Teflon<sup>®</sup> filter removed particulate  $SO_4^{2-}$ ,  $NO_3^-$ ,  $NH_4^+$ , and certain cations; and the nylon filter removed  $HNO_3$ . The Whatman filter, a cellulose fiber base impregnated with potassium carbonate ( $K_2CO_3$ ), removed  $SO_2$ . Two Whatman filters were used. In practice, a fraction (usually < 20%) of ambient  $SO_2$  is captured on the nylon filter. The nylon filter  $SO_2$  and Whatman filters  $SO_2$  were summed to provide weekly average concentrations. The nylon filter  $HNO_3$  was converted to  $NO_3^-$  and added to the  $NO_3^-$  collected on the Teflon<sup>®</sup> filter to provide weekly total  $NO_3^-$  concentrations.



**Figure 1-2.** Diagram of Three-Stage Filter Pack

Filter packs were prepared and shipped to the field weekly and exchanged at each site every Tuesday. Filter pack sampling and  $O_3$  measurements were performed at 10 meters (m) using a tilt-down aluminum tower. Filter pack flow was maintained at 1.50 liters per minute (Lpm) at eastern sites and 3.00 Lpm at western sites for standard conditions of 25 degrees Celsius ( $^{\circ}C$ ) and 760 millimeters of mercury (mm Hg) with a mass flow controller (MFC).

Ambient  $O_3$  concentrations were measured via ultraviolet (UV) absorbance. Zero, precision [90 parts per billion (ppb)], and span (400 ppb) checks of the  $O_3$  analyzer were performed every Sunday using an internal  $O_3$  generator.

CASTNet QA procedures for the EPA  $O_3$  analyzers are different from the EPA requirements for State and Local Monitoring Stations (SLAMS) monitoring as described in 40 Code of Federal Regulations (CFR) Part 58, Appendix A (EPA, 1998b). On the other hand, the QA procedures for the  $O_3$  analyzers at NPS sites meet SLAMS requirements.

Each CASTNet site employs meteorological equipment to measure temperature, delta temperature, relative humidity, solar radiation, scalar and vector wind speed, sigma theta, surface wetness, and precipitation. CASTNet meteorological measurements are described in the QAPP (Harding ESE, 2001b). The data are archived as hourly averages.

All field equipment was subjected to semiannual inspections and multipoint calibrations using standards traceable to the National Institute of Standards and Technology (NIST). Results of field calibrations were used to assess sensor accuracy and flag, adjust, or invalidate field data. In addition, audits were performed annually by Air Resource Specialists, Inc. (ARS). Results of 2000 QA activities and an assessment of data quality are discussed in Chapter 6.

## Laboratory Operations

Filter pack samples were loaded, shipped, received, extracted, and analyzed by Harding ESE personnel at the Gainesville, FL laboratory.

Following receipt from the field, exposed filters and blanks were extracted and then analyzed for  $SO_4^{2-}$  and  $NO_3^-$  by ion chromatography (IC); for  $NH_4^+$  by the automated indophenol method; and for four cations ( $Ca^{2+}$ ,  $K^+$ ,  $Mg^{2+}$ , and  $Na^+$ ) using inductively coupled argon plasma – atomic emission spectroscopy (ICAP-AE). All analyses were completed within 72 hours of filter extraction.

Results of all valid analyses were stored in the laboratory data management system [Chemical Laboratory Analysis and Scheduling System (CLASS<sup>™</sup>)]. Atmospheric concentrations were calculated based on volume of air sampled, following validation of hourly flow data.



## Methods of Data Analysis

### Modeling Dry Deposition

The original network design was based on the assumption that dry deposition or flux could be estimated as the linear product of ambient concentration (C) and  $V_d$ :

$$Flux = \overline{C} \times \overline{V_d}$$

where the overbars indicate an average over a suitable time period (e.g., 1 hour).

The influence of meteorological conditions, vegetation, and chemistry is simulated by  $V_d$ . Dry deposition processes are modeled as resistances to deposition:

$$R = R_a + R_b + R_c = 1/V_d$$

where  $R_a$  signifies aerodynamic resistance or the resistance to turbulent vertical transport;  $R_b$  is the boundary layer resistance to vertical transport in a very shallow layer adjacent to the surface; and  $R_c$  is the canopy resistance or the resistance to pollutant uptake by the vegetative canopy.  $R_c$  simulates several physical and chemical processes.

The MLM software code was updated recently according to established version control procedures (Harding ESE, 2001b). The most recent software is designated as Version 2.3.

*MLM calculations are not one-dimensional, but applied through a 20-layer canopy in which model parameters are modified by the redistribution of heat, momentum, and pollutants.*

The meteorological variables used to determine  $R_a$  and  $R_b$  were obtained from the 10-m meteorological tower at each of the sites, which is normally located in a clearing over grass or another low vegetative surface. Data on vegetative species, leaf area index (LAI), and percent green leafout were obtained from site surveys and observations by the site operator. LAI measurements were taken during 1991, 1992, and 1997 at times of summer maximum leafout. LAI values used in the MLM were extrapolated from these measurements using percent leafout observations. The resistance terms ( $R_a$ ,  $R_b$ , and  $R_c$ ) were calculated for each

chemical species and major vegetation/surface type for every hour with valid meteorological data. The  $V_d$  for a site was then calculated as the area-weighted  $V_d$  over vegetation types within 1.0 kilometer (km) of the site.

### Deposition Flux Calculations and Aggregations

Hourly deposition fluxes were calculated as the product of the hourly  $V_d$  obtained from the MLM and the corresponding hourly concentration. Hourly concentrations were obtained from the weekly filter pack results and measured hourly  $O_3$  concentrations; all hourly concentrations during a filter pack sampling period were assumed to be equal to the filter pack sample concentration and constant for the duration of the sample.

Weekly deposition fluxes are the sum of the valid hourly fluxes for a standard deposition week, divided by the ratio of valid hourly fluxes to the total number of hours in the standard week to account for missing or invalid values. A standard deposition week is defined as the 168-hour period from 0900 Tuesday to 0900 the following Tuesday. For some weeks, the filter pack sampling period did not correspond exactly with the standard deposition week, resulting in some deposition weeks being derived from hourly concentrations from more than one filter pack sample. A weekly deposition flux is considered valid if it is comprised of valid hourly values for at least 70 percent of the 168-hour week (i.e., 118 hours).

Similarly, quarterly fluxes are calculated from weekly values, and are considered valid if they are comprised of valid weekly values for approximately 70 percent of the weeks of the 13 week period. Also, the midpoint of the sampling week had to occur in the quarter to be included as part of the respective quarterly average. Annual values are calculated from quarterly values, and are considered valid if they are comprised of at least three valid quarters.

Quarterly and annual mean concentrations are aggregated based on the same requirements as the flux aggregations. However, the concentrations are averaged while the fluxes are summed.

**Figure 1-3.** Reference Sites

### ***Reference Sites Used in Trend Analyses***

One of the major goals of CASTNet is to monitor trends in air quality and deposition. Figure 1-3 presents a map of the locations of the 34 eastern sites used to perform trend analyses of pollutant concentrations from 1990 through 2000. The map also shows six western sites having 11-year data records that were used to show differences in concentration. The reference sites shown in Figure 1-3 were selected using criteria similar to those used by EPA in its National Air Pollutant and Emissions Trends Report (2000). Sites with complete data for 8 of the 10 years were selected. Missing quarterly data were interpolated from adjacent quarterly data, e.g., first quarter 1996 data were interpolated from 1995 and 1997 first quarter data. Missing quarterly means for 1990 or 2000 were assumed equal to adjacent quarterly values. A valid quarterly mean was based on eight valid weeks. Annual means were based on data from four valid quarters.

### **CASTNet Database**

The CASTNet database is available to the public via EPA's CASTNet data web page: [www.epa.gov/castnet/data.html](http://www.epa.gov/castnet/data.html). The web site provides archives of the concentration and deposition data in quote comma delimited ASCII files compressed using the PKZIP compression utility. Fully validated data are generally available approximately ten months following collection. Other documentation for the network, including information about all CASTNet sites, can be found at the CASTNet home page: [www.epa.gov/castnet/](http://www.epa.gov/castnet/).

The different types of data are archived in various tables. For example, continuous data, found in the METDATA table, consist of the following parameters:

- temperature
- difference in temperature between 2 and 9 meters
- solar radiation
- relative humidity
- ozone
- precipitation

- scalar wind speed
- vector wind speed
- wind direction
- standard deviation of the wind direction within the hour
- rate of flow through the filter pack
- wetness

*The CASTNet database contains archives of continuous meteorological, ozone, and flow data, concentrations measured on exposed filters, and MLM output of hourly, weekly, quarterly, and annual dry deposition fluxes.*

Concentration data from the dry deposition network, found in the DRYCHEM and DRYCHEM\_DAYNIGHT tables, consist of the following analytes:  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$  from the Teflon<sup>®</sup> filter,  $\text{HNO}_3$  and  $\text{SO}_4^{2-}$  from the nylon filter, and  $\text{SO}_2$  from the Whatman filters. These concentrations are maintained as micrograms per cubic meter ( $\mu\text{g}/\text{m}^3$ ).

Tables containing output from the MLM (VELHR, VELWK, VELQR, and VELAN) hold simulated deposition velocities in centimeters per second (cm/sec) for  $\text{SO}_2$ ,  $\text{HNO}_3$ ,  $\text{O}_3$ , and particles ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$ ); concentrations for the six analytes in  $\mu\text{g}/\text{m}^3$  (except for  $\text{O}_3$  with units of ppb); and modeled estimates of dry deposition for the six analytes in kilograms per hectare (kg/ha).

Finally, the VISCHEM table contains concentrations from aerosol sampling (Chapter 5) consisting of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  as measured from the denuder/nylon filter pack, carbon values as collected on the quartz fiber filter, and fine mass and trace/crustal elements as measured from the Teflo<sup>®</sup> filter. Units for  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , fine mass, and carbon samples are in  $\mu\text{g}/\text{m}^3$  and trace/crustal element samples are in nanograms per cubic meter ( $\text{ng}/\text{m}^3$ ). Continuous data from the eight visibility sites are found in the VISFLOW table and include three rates of flow: one for each type of filter pack installed at the site.

## SO<sub>2</sub> and NO<sub>x</sub> Emissions

Total annual  $\text{SO}_2$  and  $\text{NO}_x$  emissions data by state were obtained from EPA for the period 1990 through 2000. The primary purpose for presenting the emissions data is to compare trends in concentrations/depositions with trends in emissions. Also, maps of state emissions for 2000 provide context to the geographic distribution of measured concentrations and depositions.

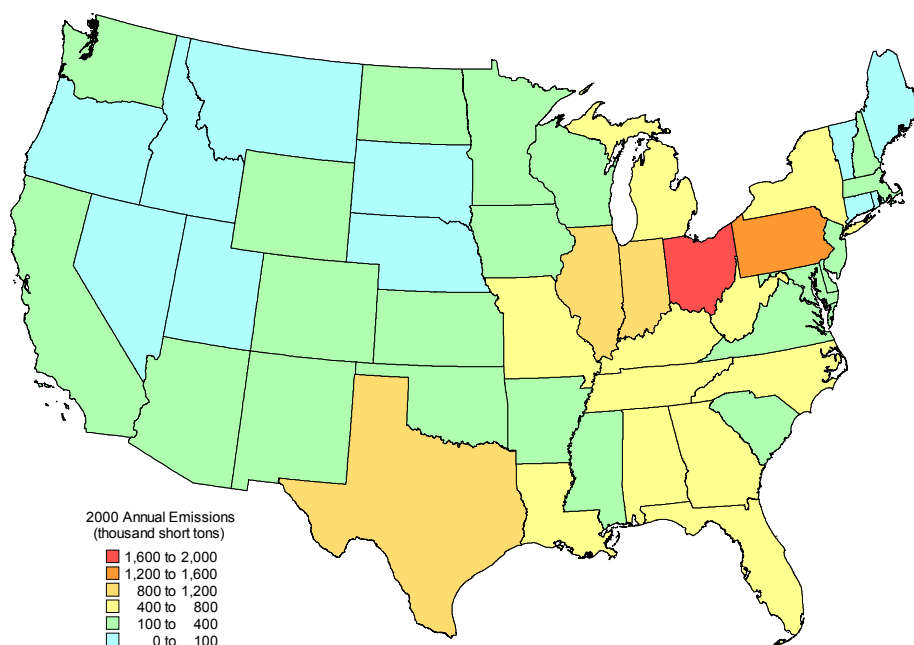
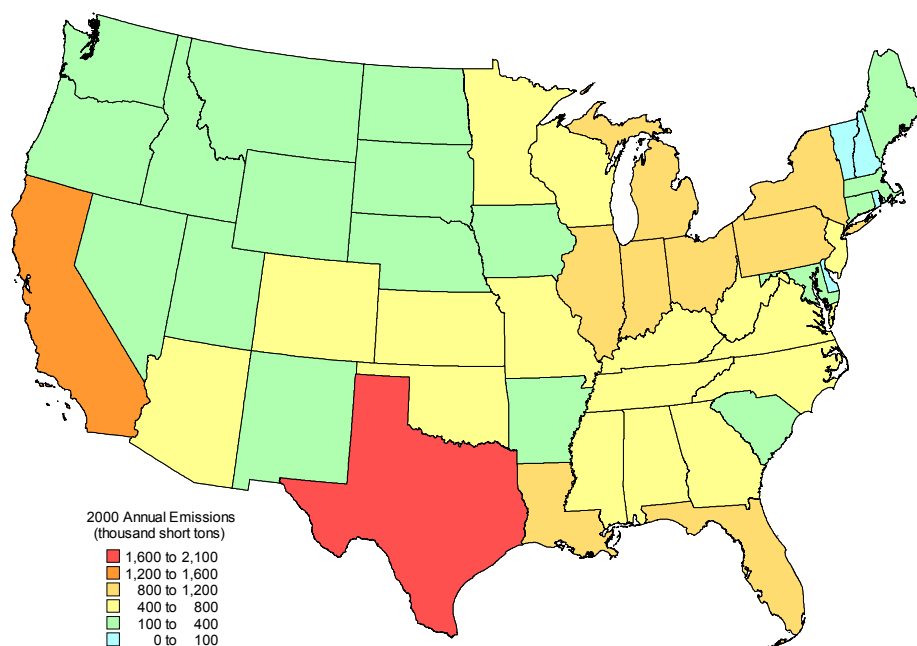
Figure 1-4 presents information on state-by-state total annual  $\text{SO}_2$  emissions for 2000.  $\text{NO}_x$  emissions are presented in Figure 1-5.

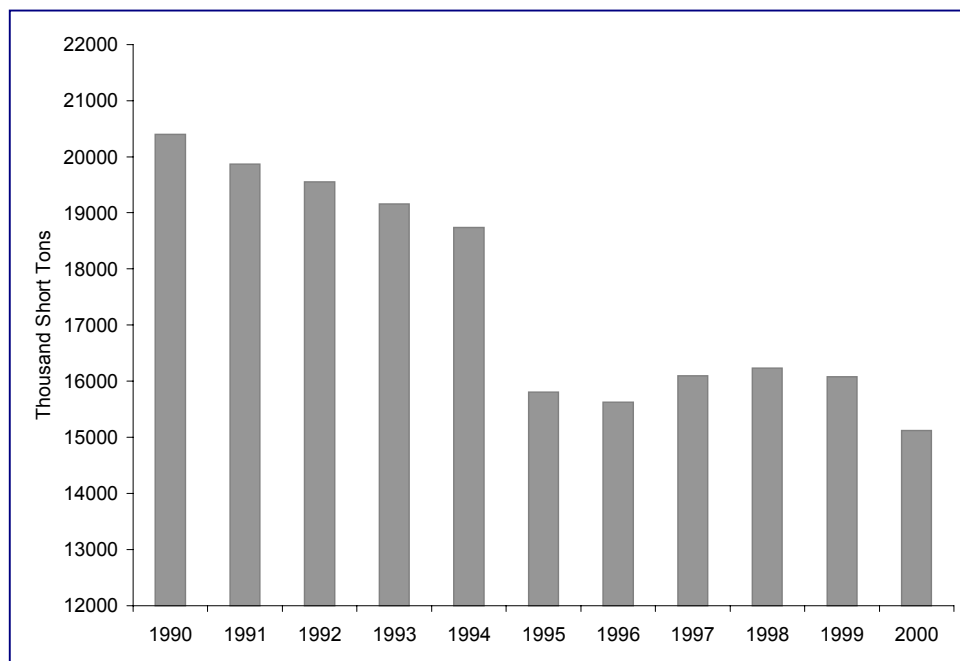
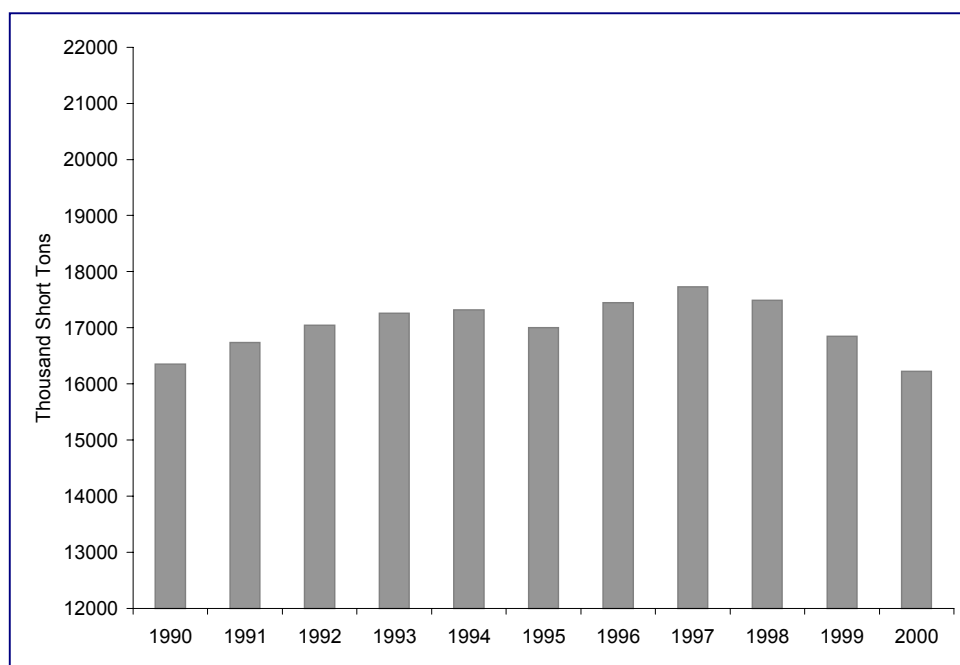
EPA prepared the emissions data as part of the National Emission Inventory (NEI) effort. EPA provided state-level summary values in order to ensure the most current information was used in this report. The state totals were calculated by summarizing individual point sources, county-level area sources, and mobile sources. EPA's methods and the availability of the data can be found on the following web site: [www.epa.gov/ttn/chief/net/index.html](http://www.epa.gov/ttn/chief/net/index.html).

Figures 1-6 and 1-7 present information on trends in  $\text{SO}_2$  and  $\text{NO}_x$  emissions over the period 1990 through 2000. Each bar on the two plots represents total annual emissions for states east of and including the north-south line of states from Minnesota to Louisiana. In other words, each bar represents the sum of emissions from the eastern states for that year. Figure 1-6 shows a sharp decline in  $\text{SO}_2$  emissions in 1995 that was produced by emission reductions at Phase I electric generating plants. Figure 1-7 depicts no overall trend in  $\text{NO}_x$  emissions but evidence of a decline over the last three years.

*SO<sub>2</sub> emissions in the eastern U.S. declined sharply in 1995 as the result of mandated emission reductions at Phase I electric generating plants. Emissions have declined over the last two years as emission reductions are implemented at Phase II plants. NO<sub>x</sub> emissions remained essentially constant over the 11-year period although a decline has been observed over the last three years.*



**Figure 1-4.** Annual SO<sub>2</sub> Emissions for 2000**Figure 1-5.** Annual NO<sub>x</sub> Emissions for 2000

**Figure 1-6.** Trend in SO<sub>2</sub> Emissions for the Eastern United States**Figure 1-7.** Trend in NO<sub>x</sub> Emissions for the Eastern United States

*Each bar represents total annual emissions for states east of and including the north-south line of states from Minnesota to Louisiana.*